## **Isomerism**

## Isomers are molecules that have the same **molecular** formula (a formula that shows the type and number of atoms in a molecule) but different **structural** formulae (a formula that shows which atoms are bonded to which and there arrangement in space). There are two types of isomerism.

**Isomerism**

**Structural isomerism**

**Stereo isomerism**

**Structural Isomers** (also called **constitutional isomers**) are molecules that have the same **molecular** formula *but* a different structural formula.

E.g. C5H12

|  |  |
| --- | --- |
| Isomer | BP oC |
|  | 36.1 |
|  | 28 |
|  | 9.5 |

Because of their different structure, these isomers have different physical properties (m.p., b.p., solubility etc), and may have different chemical properties (particularly if the structural isomers have different functional groups such as CH3COCH3 and CH3CH2CHO).

**Stereoisomerism**

There are two types of stereoisomerism.

**Stereo-isomers**

**Geometrical (cis-trans) isomers**

**Optical isomers**

**(enantiomers)**

**Geometrical isomerism** was covered in Year 12 Chemistry.

### Optical Isomers or Enantiomers

Optical isomers are also examples of stereoisomers. The enantiomer and its mirror image are non-identical. All amino acids, (except the simplest amino acid, glycine), are optically active.

This means they contain an **asymmetric**, or **chiral**, carbon atom. This is a carbon atom which has four different groups attached.

To show the different enantiomers of a molecule it is necessary to draw a 3-dimensional structure.

For any enantiomer the structure of the mirror image can be drawn by swapping **any two** groups.



Enantiomers have identical physical properties (melting point, solubility etc) BUT differ in that they **rotate** plane polarised light in opposite directions.

Optical isomers also have identical chemical properties except in their reactions with other optical isomers. This has important consequences in biochemistry where only one of the optical isomers of each amino acid occurs commonly.

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**Functional Group Chermistry**

**1. Alcohols (alkanols) - ROH, where functional group is OH.**

Named by changing “-e” at end of the alkane to “-ol”. The chain is numbered from the end giving the OH the lowest number. Alcohols are classed as primary, secondary and tertiary in the same way as the haloalkanes ie. depending on the number of C atoms that are attached to the C carrying the OH group.

Primary RCH2OH (and methanol), Secondary R2CHOH,

Tertiary R3COH.

Small alcohol molecules are polar and are highly soluble in water. However as the length of the non-polar hydrocarbon chain increases this solubility in water decreases.

Aqueous solutions are **neutral.** **Alcohols are formed** by

1. **(nucleophilic) substitution** of OH*−* for X*−* on haloalkanes
2. **addition** of H2O to alkenes.

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**Reactions of alcohols** are:

1. **elimination (or dehydration) -** forming an alkene and water

concH2SO4/heat

→ CH3CH=CH2 + H2O



propan-2-ol propene

With an unsymmetrical alcohol, the major product can be predicted using ‘the poor get poorer’ where ‘wealth’ is measured by how many H atoms are attached to the C atoms that are adjacent to the C atom to which the OH group is bonded.

concH2SO4/heat

→



CH3CH=CHCH3 + H2O

butan-2-ol but 2 ene

(major product)

**(b) Substitution -** of the OH− by a Cl*−* to form a chloroalkane.

This substitution is faster for tertiary alcohols than for secondary, and slowest for primary alcohols.

It is the basis of the **Lucas test** for distinguishing between small molecules of primary, secondary and tertiary alcohols. The reagent used is conc HCl and anhydrous ZnCl2 (called Lucas Reagent). The haloalkane formed is nonpolar and insoluble in the aqueous solution so forms a cloudy emulsion that separates out as two layers.

(i) For tertiary alcohols - solution rapidly goes cloudy and two layers form.

(ii) For secondary alcohols - solution slowly goes cloudy as the chloroalkane slowly forms and separates.

conc HCl/ZnCl2



→



(iii)No reaction with primary alcohols.

Substitution of alcohols can also be carried out using **PCl5, PCl3 and SOCl2.**

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**(c) Oxidation -** using acidified KMnO4 or acidified K2Cr2O7

The type of product formed depends on whether the alcohol used in the oxidation reaction is primary, secondary or tertiary.

1. **Primary alcohols** (RCH2OH)are oxidised to form **aldehydes** (RCHO), which are then easily oxidised further to form **carboxylic acids** (RCO2H)**.**

Cr2O72−/H+

Cr2O72−/H+



CH3CH2OH → →



ethanoic

acid

ethanal

ethanol

When using acidified dichromate in this redox reaction, the Cr2O72− is reduced to Cr3+, and the colour changes from orange to green.

1. **Secondary alcohols** (R2CHOH)are oxidised to **ketones** (R2CO)

MnO4− /H+



→

propan-2-ol propanone

(also called acetone)

When using acidified permanganate in this reaction, the purple MnO4- ion is reduced to the colourless Mn2+ ion.

1. **Tertiary alcohols - DO NOT REACT** with oxidising agents. This means these oxidation reactions can be used to distinguish tertiary alcohols from primary and secondary alcohols.

If an alcohol is heated with either acidified potassium dichromate or acidified potassium permanganate, and a colour change is observed in the oxidising agent (orange to green, or purple to colourless) then the alcohol must be either primary or secondary.

If the aldehyde is the desired product in the oxidation of a primary alcohol, the oxidising agent must be added slowly and the aldehyde distilled off as it forms. This works because the aldehyde has a lower boiling point than the alcohol and carboxylic acid as both the latter two compounds are not only polar but are capable of intermolecular hydrogen bonding. The aldehyde is a polar molecule but as it does **not** have an H atom attached to an O atom, it therefore does not have hydrogen bonding between its molecules.

If the carboxylic acid is the preferred product then the oxidising agent is **refluxed** with the alcohol to ensure complete reaction.



Reflux is a system of heating the solution with a condenser attached to the reaction vessel so that any organic substance which evaporates will be condensed and returned to the container. This way the reaction can be heated for a period of time increasing the rate of reaction without the organic substance (reactant, product or solvent) evaporating away.

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**2. Aldehydes (alkanals - RCHO) and ketones (alkanones - RCOR')**



butanal pentan-2-one

Aldehydes are named by changing “-e” at the end of the alkane to “-al”, and ketones by changing “-e” to “-one”.

Ketones (apart from propanone and butanone where there is no choice) need a number to indicate the position of the carbonyl (C=O) group.

**Oxidation of aldehydes**

Aldehydes are readily oxidised by even mild oxidising agents such as Ag(NH3)2+ (Tollens reagent)and Cu2+, (Benedicts solution) which are too weak to oxidise alcohols.

Like alcohols they are also oxidised by acidified potassium dichromate and acidified potassium permanganate.

Ketones are not oxidised, and this means that they can be distinguished by observing the reaction with an oxidising agent.

(a) **Tollens’ test** – Tollens reagent contains Ag(NH3)2+. If Tollens’ reagent (a colourless solution) is heated with an aldehyde a redox reaction occurs, which produces a silver mirror on the inner surface of the test. The aldehyde is oxidised to a carboxylic acid. The reduction half-equation is Ag+*(aq)* + e− → Ag*(s)*

If Tollens’ reagent is heated with a ketone or an alcohol no reaction occurs.

(b) **Benedict's test** - Benedict’s reagent is a solution containing a copper(II) citrate complex ion. When Benedict’s solution is heated with an aldehyde the blue complex of Cu2+ is reduced to a **brick** **red precipitate of Cu2O**.

When heated with a ketone (or an alcohol), Benedict’s solution does not react and remains blue.

(c) **Acidified dichromate and acidified permanganate**  -oxidise aldehydes to carboxylic acids (colour changes are orange Cr2O72-/H+ to green Cr3+, and purple MnO4-/H+ to colourless Mn2+).

These reagents can be used to distinguish between aldehydes and ketones, but not between alcohols and aldehydes.

This space is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

*Exercise*

*Name the organic products formed in each of the following reactions. In some cases there will be no reaction.*

*(a) Methanal is heated with Tollens reagent.*

*(b) 2-Propanol is heated with Benedict’s reagent*

*(c) Propan-1-ol is reacted with acidified potassium permanganate*

*(d) 2-methyl-2-propanol is heated with Cr2O72*−*/H+*

*(e) 3-methyl pentanal is reacted with Benedict’s reagent.*

*(f) Butanone is heated with Tollens reagent.*

**3. Haloalkanes (alkyl halides) RX where X = F, Cl, Br, I**

Named as a chloroalkane or bromoalkane etc, with the position of the halogen given by the appropriate number of the carbon that it is attached to in the chain.

The haloalkanes can be classified as

1. primary R**C**H2X - the C atom to which X is attached is only attached to one or no other C atom
2. secondary R2**C**HX - the C atom to which X is attached is attached to two other C atoms

* tertiary R3**C**X - the C atom to which X is attached is attached to three other C atoms.

Haloalkanes are relatively nonpolar overall (despite the polarity of the C-X bond) and are insoluble in water.

A monohaloalkane eg. 2-bromopropane can be formed by

a) addition of HBr to propene (forming only one product)

**or**

b) substitution of propane using Br2. (forming two products, the bromoalkane and HBr)

**or**

c) substitution of the OH on an alcohol using eg. PCl3, PCl5,SOCl2 or conc HCl/ZnCl2

### Substitution Reactions of Haloalkanes, RX

Haloalkanes undergo reaction by **substitution** (replacing the X- with another group)**.** This can be doneusing aqueous **OH- or H2O** to produce an **alcohol** (or by using ammonia to produce an amine). e.g.

+ OH-→ + Br-



2-bromopropane propan-2-ol

**Elimination Reactions of Haloalkanes**

Elimination isfavoured when the solvent used is less polar eg. alcoholic (rather than aqueous) **KOH.**

The reagent may be referred to as either KOH / CH3CH2OH or OH- in alcohol.

(KOH/ethanol)

→ CH3CH=CH2 + HBr



With an unsymmetrical alcohol, the major product can be predicted using ‘the poor get poorer’ where ‘wealth’ is measured by how many H atoms are attached to the C atoms that are adjacent to the C atom to which the OH group is bonded.

(KOH/ethanol)



→ CH3CH=CHCH3 +

H2O

but 2 ene

major product

2 chloro butane

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

*Exercise*

*Give the major organic product for each of the following reactions.*

*a) OH−(aq)*

→



*b)*



*OH− / alcohol*

→

**4. Amines (aminoalkanes)**

Amines are named as substituents eg aminomethane, CH3NH2. These may be classed as primary, secondary or tertiary, but unlike the haloalkanes the classification depends on the number of C atoms attached to the N atom.

**Primary RNH2, secondary R2NH, tertiary R3N.**

Amines have an unpleasant “fishy” smell. The smaller amines, up to C5, are soluble in water but larger alkanes are insoluble, as the size of the non-polar hydrocarbon chain cancels out the effect of the polar amino functional group.

Like ammonia itself, water soluble amines form alkaline solutions. They react with water by proton transfer to form OH- ions.

This means aqueous solutions of amines turn litmus blue.

RNH2 + H2O → RNH3+ + OH*−*

Amines also react with acids to form salts.

CH3NH2 + HCl → CH3NH3+Cl*−*

aminomethane methyl

ammonium chloride

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**5. Carboxylic acids – (alkanoic acids –RCOOH)**



Carboxylic acids contain the functional group

They are named by changing the “-e” on the parent alkane to

“-oic acid”. Acids taste sour. Organic acids are weak acids - the smaller molecules dissolve in water and react by donating a proton to the water. This means aqueous solutions turn litmus red.

CH3COOH + H2O sm eq arrow CH3COO− + H3O+

eth**anoic** acid eth**anoate** ion

**Substitution reactions.**

Carboxylic acids can react by **substitution** of the **OH−** to form

1. acid chlorides, RCOCl
2. esters, RCO2R’
3. amides, RCONH2
4. Using PCl3, PCl5 or SOCl2 (not conc HCl), carboxylic acids undergo a substitution reaction to form **acid chlorides, RCOCl**.



PCl5



→

eth**anoic acid** eth**anoyl chloride**

Using alcohols and conc H2SO4 as a catalyst, carboxylic acids undergo a substitution reaction to form **esters, RCO2R’**.



Conc H2SO4

sm eq arrow+ CH3OH

+ H2O

ethanoic acid methanol methyl

ethanoate

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**6. Acid Chlorides - RCOCl**

Acid chlorides are highly reactive and are the preferred starting point for the formation of carboxylic acid derivatives i.e. esters and amides (including substituted amides).



1. They react violently with water, forming white fumes of HCl.

CH3COCl + H2O → CH3CO2H+ HCl

(b) They react with ammonia to form amides

CH3COCl + NH3 → CH3CONH2+ HCl

(c) They react using amines to form **N-substituted amides**

CH3COCl +CH3NH2 →

methanamine

CH3CONHCH3 + HCl

N methyl ethanamide

(d) Rapid reaction of **alcohol + acid chloride** to produce an ester + HCl. No acid catalyst required.

CH3COCl +CH3OH →

methanol

CH3CO2CH3 + H2O

methyl ethanoate

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**7. Esters – RCOOR’**

The ester functional group is where R and R1 are alkyl groups, although R can be an H atom.



Esters may be identified by their fruity smell. In aqueous solution esters are neutral. They are named as alk**yl** alk**anoates**, where the alkyl part is derived from the alcohol, and the alkanoate from the carboxylic acid used to make the ester. Esters are formed by

1. the acid catalysed reaction of **alcohol + carboxylic acid** to produce an ester + water.

(conc H2SO4)

CH3(CH2)2CO2H +CH3OH →

butanoic acid methanol

CH3(CH2)2CO2CH3 + H2O

methyl butanoate

1. Rapid reaction of **alcohol + acid chloride** to produce an ester + HCl. This reaction does not require an acid catalyst.

### Hydrolysis of an ester

The hydrolysis of an ester in aqueous solution results in the break up of the ester and the formation of an alcohol and the carboxylic acid or carboxylate ion (depending on the pH of the solution).

1. Hydrolysis in acid produces the alcohol + carboxylic acid.

CH3CH2COOCH3 + H2O / H+ →

methyl propanoate

CH3CH2COOH + CH3OH

propanoic acid methanol

Hydrolysis in NaOH soln gives alcohol + **sodium salt** of the carboxylic acid.

CH3CH2COOCH3 + NaOH →

methyl propanoate

CH3CH2COONa + CH3OH

sodium propanoate methanol



The alcohol is separated from the sodium salt by distilling it off using the equipment shown. Water runs through the outer case of the condensor to cool any alcohol vapour.

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**Fats and oils**

Fats and oils are esters of glycerol (propane-1,2,3-triol) combined with long chain carboxylic acids (fatty acids). They are triesters or triglycerides. Oils generally originate from plant sources and fats from animal sources. Oils have a lower melting point because their fatty acid chains contain a number of double bonds (i.e. they are “polyunsaturated”). The *cis-* isomer formed results in a shape where the molecules cannot pack together as closely so the intermolecular attractions are weaker. Oils can be converted into “harder” fats (e.g. margarine) by partially hydrogenating some of these double bonds.

Hydrolysis of simple esters in acidic conditions breaks down the esters to form the alcohol, glycerol, and the carboxylic acids. Hydrolysis in basic conditions such as aqueous sodium hydroxide, produces glycerol and the sodium salts of the fatty acids. In the formulae below the R represents long hydrocarbon chains, either saturated or unsaturated.

The sodium salts of the fatty acids are used as soaps.



+ 3NaOH

→

+ 3RCO2Na

**8. Amides - RCONH2**

Amides are solids. They have no smell and aqueous solutions are neutral (NOT basic). They are named by changing “-e” to “-amide”.

They are formed by **substitution reaction of acid derivatives.**

(a) acid chloride + ammonia →

heat

amide + HCl (rapid reaction)

(b) ester + ammonia → amide

+ alcohol (slow reaction)



**9. Amino acids**

General formula



aminoethanoic acid (glycine)

2-aminopropanoic acid (alanine)

Amino acids have both the basic amino, NH2, and acidic carboxylic acid, CO2H, groups. In acidic solutions, the basic NH2 group is protonated to form a positively charged amino acid.



+ H3O+ →



+ H2O

In alkaline solution, the carboxylic acid group loses a proton forming a negatively charged ion.



+ OH− →



+ H2O

This page is for your summary notes

|  |
| --- |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |
|  |

**10. Condensation polymers**

A condensation reaction involves two or more molecules combining to form a larger molecule and a small molecule such as H2O or HCl. The two types of condensation polymers are **polyesters** (nylons) and **polyamides** (including proteins).

**Polyesters** are formed by the reaction between either

a) a diacid and a dialcohol →

polyester + water

n(HO2C-(CH2)6-CO2H)+n(HO-(CH2)6-OH) → -C-(CH2)6-C-O(CH2)6O- + nH2O

|| ||

O O

b) a diacid chloride and a dialcohol →

polyester + HCl

n(ClOC-(CH2)6-COCl) + n(HO-(CH2)6-OH)

→ -C-(CH2)6-C-O(CH2)6O- + nHCl

|| ||

O O

**Polyamides**  are formed by the reaction between a

diacid (or diacid chloride) + diamine

→ polyamide + water

**n(HO2C-(CH2)6-CO2H) + n(H2N-(CH2)6-NH2)**

**→ -C-(CH2)6-C-NH(CH2)6NH- + nH2O**

|| ||

O O

n(ClOC-(CH2)6-COCl) + n(H2N-(CH2)6-NH2)

→ -C-(CH2)6-C-NH(CH2)6NH- + nHCl

|| ||

O O

**Proteins** areone example of a biologically important polymer. They are found in all parts of the body as they are the structural components of skin, muscle and hair, while others are enzymes that catalyse reactions in the body.

Proteins are formed by the condensation of a large number of amino acids. Small molecules called dipeptides and tripeptides are formed by the condensation of two and three amino acid molecules respectively. If two amino acids condense to form a dipeptide there are two possible distinct structures - AB and BA

→



**+**



*Exercise*

*Draw the 2 possible dipeptides that can be formed when the following 2 amino acids combine.*



*+*

When many hundreds of amino acid molecules continue linking by these condensation reactions, proteins are formed.

**Hydrolysis of Proteins and Peptides**

Hydrolysis of the protein or peptide will produce the constituent amino acids. If this is done in acid solution they will be in the form of the positive ion, whereas if it is in base solution they will be in the form of the negative ion.

#### Exercise -Draw the structures of the amino acids formed by hydrolysis of the following dipeptide in



*(a) acidic conditions*

*(b) basic conditions*